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THEORY OF STATIC FATIGUE IN BRITTLE SOLIDS.
CRACKS AND ENERGY - CRITERIA FOR BRITTLE FRACTURE

R. H. Doremus

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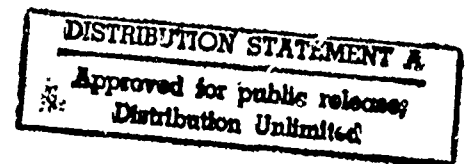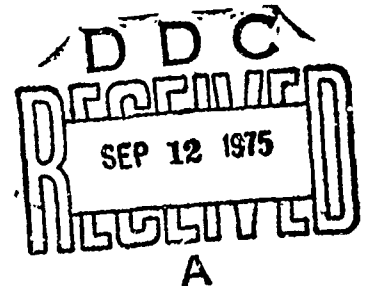R. H. Doremus

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13 ABSTRACT

Energies of cracks are considered in terms of the first and second laws of thermodynamics, and it is concluded that the Griffith criterion provides a necessary but not sufficient condition for crack propagation. Thus surface energies calculated from fracture experiments give only an upper bound to the true surface energies of solids. The correct criterion for fracture is Inglis' equation for the stress at the tip of a crack; the radius of the crack tip is a parameter that cannot be ignored in fracture experiments.

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THEORY OF STATIC FATIGUE IN BRITTLE SOLIDS

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ABSTRACT

A theory of static fatigue in brittle solids is
derived, based on the ideas of Hillig and Charles, but
using a different log reaction velocity-stress relation-
ship. The resulting equation agrees well with the
functional dependence of failure time on stress found
experimentally, and experimental values of the stress-
sensitivity factor are consistent with the theory.
Variations in failure times with sample history and
glass composition can only partly be explained by the
theory.

THEORY OF STATIC FATIGUE IN BRITTLE SOLIDS

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INTRODUCTION

Stress-accelerated reaction of water with glassy and crystalline oxides can lead to weakening and crack propagation. This phenomenon has been studied in two different ways. The time to fracture of a specimen held under a constant load gives a measure of "static fatigue", and the rate of lengthening of macroscopic (about one cm. long) cracks as a function of load demonstrates slow crack propagation. In some materials these two types of experiments seem to be closely related, such as in soda-lime glass, but in other materials such as fused silica, there are discrepancies between the two types of measurements.

Several theories of static fatigue or delayed failure of brittle solids have been proposed; that of Hillig and Charles[1] is now generally accepted. Their theory considers changes in the dimensions of cracks in a sample surface resulting from the reaction of water with the material. For example, in a silicate glass the load is born by the silicon-oxygen network. Water breaks silicon-oxygen bonds by the reaction

$$H_2O + Si-O-Si = SiOH \; HOSi, \tag{1}$$
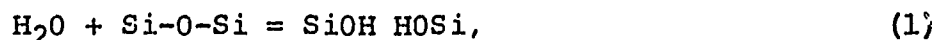
so this reaction can change the dimensions of the cracks and weaken

1.

the material.

Defects or cracks in the surface of a brittle material weaken it because stress is concentrated at the crack tip. Consider an elliptical crack of length (semi-major axis) L and half-width (semi-minor axis) a subjected to a tensile stress S perpendicular to L. Let x be the distance from the crack axis in the direction of the applied stress; x = 0 at the crack tip and x = a at the half-width of the crack. The solution to elastic deformation of the crack gives a stress σ at the crack surface distributed as follows :

$$\frac{\sigma}{S} = \frac{1+2L/a - (L+a)^2 \, x^2/a^4}{1+(L^2 - a^2) \, x^2/a^4} \quad . \tag{2}$$

At the crack tip where x = 0

$$\sigma_o = S(1+2\,L/a) \tag{3}$$

if L >> a

$$\sigma_o \approx 2S\,L/a = 2S\sqrt{L/\rho} \tag{4}$$

where $\rho = a^2/L$ is the radius of curvature of the crack tip. The stress decreases very sharply away from the tip, according to Eq. 2.

Hillig and Charles assumed that the rate of reaction of water with the material controls the change of crack dimension, and that this rate v is

$$v = v_o \exp \beta\sigma \tag{5}$$

where σ is the tensile stress at the crack tip, β is the coefficient that can be written as V*/RT, where V* is an "activation volume", and v_o is the rate of the reaction at zero applied tensile stress. At

the crack tip the rate at which the crack lengthens $dL/dt = v$, so Eq. 4 also gives the rate of slow crack propagation as a function of tip stress.

In order to relate Eq. (5) to the time of delayed failure, the tip stress σ must be expressed as a function of crack dimensions (Eq. 4). The sharp decrease of stress away from the crack tip, and the exponential relation between stress and reaction rate, mean that the tip should sharpen much more rapidly than lengthen. Thus Hillig and Charles assumed that the crack length L remains nearly constant, and only the tip radius ρ changes appreciably. With this assumption they solved Eq. 5 in terms of ρ. The crack was assumed to propagate to failure when the tip stress σ_o equaled σ_t, the ultimate or theoretical cohesive strength of the material. If the fracture strength S_N at liquid nitrogen temperature is time-independent, reaction (1) being very slow at this temperature, then from Eq. 4

$$\sigma_t = 2S_N \sqrt{L_o/\rho_o} \tag{6}$$

where Lo and ρ_o are the initial dimensions before corrosion. The final equation for fracture time t as a function of stress S was found to be, after neglect of small terms:

$$\ln t/t_{0.5} = - \beta\sigma \; (S/S_N - 0.5) \tag{7}$$

where $t_{0.5}$ is the fracture time at $S/S_N = 0.5$. The linear dependence of log fracture time on stress of Eq. 7 is found experimentally for various glasses and alumina in certain stress ranges [3-5] and is therefore taken as support of the theory.

There is some question about the assumption that L changes much less than ρ. Although this result would indeed be expected from Eqs. (2) and (5), as soon as the tip has corroded a small amount the stress distribution at the tip probably is not given by Eq. (2). A tip radius of about $20\overset{\circ}{A}$ for cracks in soda-lime glass was found in an etching study [6]. If the applied stress is $0.25\ S_N$, then the tip radius must decrease by a factor of sixteen for failure to occur, from Eq. 4. This gives a final tip radius of less than atomic dimensions, which seems unlikely. Energy considerations also indicate that this small a tip radius is unlikely [7].

To overcome these difficulties a somewhat different approach was taken [8]. One can start with Eq. 1 in the form:

$$v = \frac{dL}{dt} = v_o \exp \frac{2\beta SL}{a} \tag{1-a}$$

The assumption is made that a, rather than L, is constant with time, since the corrosion rate of the minor axis of the ellipse is much less that that of the major axis. This assumption is equivalent to assuming that the tip radius is inversely proportional to the length during corrosion, since $\rho = a^2/L$. With this assumption Eq. (7) was derived, predicting a linear dependence of $\log t$ on S/S_N. In fact a variety of assumptions about relative changes in L and ρ give this dependence; for example, if it is assumed that ρ is constant and only L changes, a linear relation between $\log t$ and S/S_N is still found.

There are some discrepancies between Eq. 7 and experimental

results on static fatigue in glasses. The factor $\beta\sigma_t$ should be invarient for a particular glass, since it includes two intrinsic parameters, β, the measure of the effect of stress on a corrosion process, and σ_t, the ultimate fracture strength of the material. Nevertheless different slopes of S/S_N versus log t plots are found for different surface treatments of the same glass, implying diffferent values of $\beta\sigma_t$ for these treatments. For example, in etched soda-lime glass[5] a value of 77 is found for $\beta\sigma_t$, compared to 31 for the data of Mould and Southwick[3]. For FN borosilicate glass different slopes are found for different surface treatments[4], and for fused silica $\beta\sigma_t$ is 31 for abraded samples and 72 for flame-polished samples[9].

Extensive delayed failure tests of soda-lime glass after different surface treatments and an analysis of distributions of failure times at a particular stress showed[10] that the log failure time is not linear with applied stress, even in the range $0.8 > S/S_N > 0.4$. Other functional dependencies were examined, and a good fit to the data was found for inverse proportionality between log failure time and stress. Such a dependence was also suggested for experimental delayed failure measurements of Baker and Preston on Glass[11,12], and by Taylor[13]. Slow crack propagation data also fit an inverse relation between log crack velocity and load better than direct proportionality[10,14]. In this paper theoretical reasons for such dependencies are explored, and the equations derived are

compared to experimental data on static fatigue.

DEPENDENCE OF REACTION RATE ON STRESS

The effect of pressure on a chemical reaction rate constant k is found from transition state theory to be[15]

$$\left(\frac{\partial \ln k}{\partial p} \right)_T = - \frac{\Delta V^*}{RT} \tag{8}$$

where ΔV^* is the difference between the molar volume of the "activated complex" of the reactants and their normal molar volumes. If ΔV^* is constant with pressure,

$$k = k_0 \exp (- p \, \Delta V^*/RT). \tag{9}$$

In the equation for the temperature dependence of a chemical reaction

$$k = k' \exp (- \Delta H^*/RT, \tag{10}$$

where ΔH^* is the activation enthalpy or energy, ΔH^* is often independent of temperature over wide ranges of temperature. However, ΔV^* is rarely independent of pressure[16,17] so Eq. 9 with ΔV^* constant cannot be considered a general relation for pressure or stress effects. Thus the assumption of Eq. 5 with β independent of stress has no experimental support.

An equation of the form

$$v = v_\infty \exp (- \alpha/\sigma) \tag{11}$$

with v_∞ and α as stress-independent coefficients, is proposed for the rate of reaction of water with oxides subjected to a tensile stress σ; v_∞ is the limiting reaction rate at high stress. Equation 11 with v as the velocity of crack propagation and σ proportional to the load fits slow crack propagation data better than Eq. 5.

Taylor[13] suggested that delayed fracture in brittle materials resulted because of a time-dependent rearrangement of the structures of the material. He found that the "activation energy for fracture" should be reduced as the bond length increased, and he assumed that water also reduced the activation energy. He derived an equation of the same form as Eq. 11 for the "rate of fracture". These ideas can be modified somewhat and applied to the present point of view to gain some possible insight into the origin of Eq. 11 and parameters affecting c. If the activation energy for reaction 1 is inversely proportional to the change in bond length Δa from the original value a_o, then

$$\frac{a}{\sigma} = \frac{B}{RT\Delta a} = \frac{BE}{RTc} \tag{12}$$

where B is a constant, so c should be proportional to Young's molulus E and inversely proportional to temperature. The constant B should be proportional to the activation energy for the reaction of water with the oxide network.

STATIC FATIGUE

If the reaction of water with an oxide as a function of stress follows Eq. 11, then from Eq. 4:

$$v = \frac{DL}{dt} = v_\infty \exp \left(\frac{ca}{2SL} \right) \tag{13}$$

Again it is necessary to make some assumption about the relative change in crack length L and tip radius ρ as corrosion proceeds. As before the assumption is made that a is constant, or that $\rho = a^2/L$

is inversely proportional to L. The particular relation assumed does not change the final equation significantly, as shown below.

In order to solve Eq. 13, the following substitution is made:

$$x = \frac{\alpha a}{2SL} \tag{14}$$

When $t = 0$, $x = x_0 = \alpha a/2SL_0$. Then Eq. 13 becomes:

$$\frac{e^x}{x^2} \, dx = - \frac{2S \, V_\infty \, dt}{\alpha a} \tag{15}$$

or integrating between $t = 0$ and $t = t$:

$$\int_{x_0}^{x} \frac{e^z dz}{z^2} = - \frac{2S \, V_\infty \, t}{\alpha a} \tag{16}$$

The integral is

$$\int_{x_0}^{x} \frac{e^z d z}{z^2} = \left[- \frac{e^z}{z} \right]_{x_0}^{x} + \int_{x_0}^{x} \frac{e^z dz}{z} = - \frac{e^x}{x} + \frac{e^{x_0}}{x_0}$$

$$+ \int_{-\infty}^{x} \frac{e^z}{z} \, dz - \int_{-\infty}^{x_0} \frac{e^z}{z} \, dz \tag{17}$$

The experimental values of x are several times larger than unity.

Under this condition the last two integrals can be expanded as follows [18]:

$$\int_{-\infty}^{x} \frac{e^z}{z} \, dz = \frac{e^x}{x} \left(1 + \frac{1!}{x} + \frac{2!}{x^2} + \frac{3!}{x^3} + \ldots \right) \tag{18}$$

The series is "semi-convergent", that is, it can be used up to those terms that begin to increase in value. If $x \gg 1$, then the approximate result for Eq. 16 is:

$$+ \frac{e^x}{x^2} - \frac{e^{x_0}}{x_0^2} = - \frac{2S \, V_\infty \, t}{\alpha a} \tag{19}$$

Since $x_0 = \alpha\, S_N/\sigma_t S$, when S/S_N is less than about 0.8, $e^x \ll e^{x_0}$, and finally

$$\exp\left(\frac{\alpha\, S_N}{\sigma_t S}\right) = \frac{V_\infty}{L_0}\, \frac{\alpha}{\sigma_t}\, \frac{S_N}{S}\, t \tag{20}$$

or $\ln t = \dfrac{\alpha/\sigma_t}{S/S_N} + \ln\left(\dfrac{S L_0 \sigma_t}{S_N V_\infty \alpha}\right)$ (21)

Since $\ln S/S_N$ varies slowly with S/S_N for $S/S_N > 0.25$, this equation gives inverse proportionality between log of the fracture time and S/S_N, as found experimentally.

Other assumptions about the relation between L and ρ as reaction proceeds give the same inverse proportionality between $\ln t$ and S/S_N as does Eq. 21. For example, if it is assumed that ρ changes much more than L, as suggested by Hillig and Charles, the exponent of x in Eq. 14 approaches one instead of two, and the final equation is

$$\ln t = \frac{\alpha/\sigma_t}{S/S_N} + \ln \frac{L_0}{V_\infty} \tag{22}$$

Alternatively if ρ is assumed to be constant and only L changes, the exponent of x in Eq. 15 becomes three, and with x large $\ln t$ is still inversely proportional to S/S_N. This same independence of the functional relation between $\ln t$ and S/S_N on the variations of L and ρ was found in the last section for the theory of Hillig and Charles. It means that the functional dependence of log t on S/S_N (or of crack velocity on load) ca not be used to decide between different geometric changes in the crack tip and length. The time t_h to

failure at $S/S_N = \frac{1}{2}$ is, from Eq. 20:

$$t_h = \frac{L_0 \sigma_t}{2v_\infty \alpha} \exp \left(\frac{2\alpha}{\sigma_t} \right)$$ (23)

STRUCTURE OF OXIDE SURFACES

In this section recent understanding of the structure of oxide surfaces, particularly of silicate glasses, is summarized, because this structure can influence the rate of reaction of water with the oxide

A fracture surface of an oxide contains "dangling" oxide bonds. These bonds react rapidly with atmospheric water to form metal hydroxyl groups such as SiOH, BOH or AlOH. In addition to these "external" hydroxyl groups a hydrated layer several atomic distances thick can be formed on the oxide surface by a reaction like that in Eq. 1. This hydrated layer is more or less porous to water, and the interface between it and the unhydrated oxide is probably the actual load-bearing point Thus a thin crack can be partially filled with a hydrated oxide.

The surface structure of a silicate glass containing alkali is even more complex. Ion exchange between alkali ions in the glass and hydrogen or hydronium ions from water can take place:

$$Na^+ + 2H_2O = H_3O^+ + NaOH$$ (24)

The resulting surface structure can be divided into layers, as shown in Fig. 1, based on the work of several different investigators[19-21].

If the glass is in contact with liquid water the outer surface

dissolves into the water; in contact with water vapor a layer of alkali hydroxide or carbonate builds up on the glass surface, speeding corrosion of the gel. Movement of the gel-glass interface results from reaction 1, and the rate of this movement can be associated with the velocity v of the previous section. Since the mobility of hydronium ions is much smaller than that of sodium or lithium ions, the layer containing hydronium ions has a much higher resistance than the unexchanged glass. On the other hand, the gel layer is quite open, so ions in it have a high mobility. These differences of conductivity of the various layers have been confirmed by Wikby[21] in measurements of the resistance of glass membranes progressively etched by HF.

COMPARISON OF EQUATIONS WITH EXPERIMENTS

In Table 1 are values of α/σ_t for various brittle materials as calculated from log failure time versus reciprocal stress plots and Eq. 21. All these plots were linear for the data in Table 1, are required by Eq. 21. Soda-lime samples treated in a wide variety of ways[3,10] all came close to the same α/σ_t values. Abraded and[4] pristine fused silica[9] showed widely different slopes on log failure time versus stress plots, but on reciprocal stress plots abut the same slopes and α/σ_t values were found[10]. For FN borosilicate glass the values of α/σ_t was dependent on treatment; the reason for this result is not known.

The theoretical fracture stress σ_t can be calculated from the

following equation[22] :

$$\sigma_t^2 = \frac{E \, U_o}{8a} \qquad (24)$$

where U_o is the potential energy per unit surface area at equilibrium separation a, and E is Young's modulus. U_o can be found from bond energies and the atomic density of the material. A σ_t of $1.3(10)^{10}$ Newtons/meter^2 $(2.6(10)^6$psi) was calculated for fused silica[22], which is not much greater than the maximum measured strength of fused silica at -196°C, or 1.4 N/m^2 $(2(10)^6$psi). For silicate glasses the various factors in Eq. 24 change little with glass composition, so σ_t should be nearly the same for most of these glasses. A value of $1.4(10)^{10}$N/m^2 $(2(10)^6$psi) is estimated for soda-lime glass.

Composition effects on α are less certain. From Eq. 12 and the discussion following it α should not change much for different silicate glasses, since Young's modulus for most of these glasses is about the same, and reaction 1 governs the destruction of the load-bearing silicate network in these glasses. Rana and Douglas[23] measured the activation energies for the linear corrosion rates of various glass, which are probably related to the activation energies for reaction 1, as described in the last section. They found activation energies from 15 to 25 kcal/mole for various soda-lime silicate glasses, so it might be reasonable to assume a value of 20 ± 5 kcal/mole.

Therefore neither α nor σ_t should change much for silicate glasses, in agreement with the similar experimental values for α/σ_t for different glasses.

The theoretical fracture strength of alumina can be calculated from Eq. 24 to be about $2.2(10)^{10} N/m^2$ $(3.2(10)^6 psi)$, or slightly larger than that of fused silica. The activation energy for the rate of reaction of water with aluminum-oxygen bonds is uncertain, but should not be too different from the 20 kcal/mole for silicates. Thus, the three-fold increase in α/σ_t found experimentally for alumina as compared to the silicate glasses probably results mainly from the higher modulus of alumina, which is about six times greater than those of silicate glasses.

These comparisons show that the values of α/σ_t found experimentally are in reasonable accord with theoretical values, and lend support to the present derivation.

Values of t_n for a particular material treated in different ways vary widely. For soda-lime glass values of t_n differ by three orders of magnitude depending upon the history and type of abrasion.[3,10] The t_n values for abraded and pristine fused silica diverge by about eight orders of magnitude[4,9]. Between alumina samples as-received and samples heated through several cycles up to about 1200°C, there was a difference of about two orders of magnitude in t_n. These variations cannot be readily explained by Eq. 23.

One would expect α/σ_t for a particular material to be

independent of treatment, as is generally found experimentally, with the exceptions noted in Table 1.

Differences in initial crack length L_0 can be deduced from sample strengths. The different treatments of soda-lime glasses led to variations of about a factor of two in liquid nitrogen strength. Thus the initial crack lengths should vary at the very most by an order of magnitude, since the radius ρ of the crack tip does not usually change much. The pristine silica had a strength at liquid nitrogen temperature about 100 times greater than the strength of abraded fused silica at this temperature. Thus L_0 for abraded silica could be four or five orders of magnitude greater than for pristine, but not eight orders of magnitude. The liquid nitrogen strength of heated alumina was about 1.5 times that for as-received samples; again the initial crack length L_0 should vary much less than found experimentally for t_n.

The influence of various treatments on the reaction rate v_∞ at high stress is uncertain. One would expect v_∞ to be proportional to water concentration (humidity). The results discussed here were carried out either in water or 100%, or 50% relative humidity, which should result in changes of no more than a few times in v_∞. For fused silica and alumina v_∞ could be influenced by the thickness of hydrated layer on the oxide surface, but the extent of such influence is uncertain.

The layer structure of surfaces of alkali silicate glasses,

described in the last section, could influence v_∞ more strongly.
In a very thin crack near its tip products of alkali-hydronium ion
exchange (reaction 24) could build up, and the alkali hydroxide
increase v_∞ substantially. Various treatment. could influence the
basicity at the tip, changing v_∞. The thickness of a pre-existing
layer of hydrated glass in the crack could also influence the rate
of ion exchange, thus changing the alkalinity and v_∞. The extent
of such influence and whether or not it can explain the large
experimental changes in t_n await more detailed experiments on the
relation between the structure of the hydrated layer and its
dissolution rate in water.

With the large uncertain changes in t_n for a particular
material it would seem audacious to try to explain differences in
t_n between different materials. However, for certain materials
treated in the same way there seems to be some relation between t_n
and the chemical durability of the material. In Table II are
listed the t_n values for three glasses and alumina that had been
centerless ground or abraded. The strengths of the glasses were
all about the same, and they have about the same c/σ_t values (see
Table I). Thus from Eq.23 any large differences in t_n for the glasses
should result from differences in v_∞.

Measurements of the rate of dissolution of some glasses have
been made by various authors, and some of these results are given
in Table III.

Douglas and co-workers[23,26] found that alkali-silicate glasses

dissolve in two stages. During the first the rate of dissolution

is proportional to the square root of time, whereas during the

second the rate is directly proportional to time. The rate in the

first stage is controlled by interdiffusion of alkali and hydronium

ions, and the second is a steady-state condition in which the rate

is controlled by dissolution of the silicate network of the glass[19,7].

Thus the rate of dissolution during the second stage corresponds to

the movement of the gel-glass interface described in the last

section (see Fig. 1). For sodium and potassium silicate glasses

containing a variety of third oxides, including alkaline earths,

aluminum, zirconium, lead, and zinc, the rate of dissolution during

the second stage at 100°C varied by no more than a factor of

twenty[26], and most of these values were lower than that for soda-

lime glass given in Table III.

From the data in Table III one can conclude surprisingly that

the rate of dissolution of silica in water is about the same as

that of alkali silicate glasses. Therefore if v_∞ shows the same

changes with glass composition as these dissolution rates, the

differences in t_n values between fused silica and soda-lime glass

cannot be explained by changes in dissolution rate. There is an

unexplained difference of four to seven orders of magnitude between

t_n for silica and for soda-lime glass.

Some theories for the rate of reaction of water at crack tips

in glasses have been proposed[27,28], but they do not take into
account the hydrated layer or the details of surface structure
given in the last section and Fig. 1. Furthermore they cannot
explain the experimental variations of t_n with humidity, heat-
treatment, type of abrasion, and glass composition.

CONCLUSIONS

The present theory is claimed to be an improvement over that
of Hillig and Charles because it removes some of the inconsistencies
described in the introduction. The functional dependence of log
failure time on stress in static fatigue experiments fits Eq. 21
derived here better than previous equations and the parameter σ/σ_t
found experimentally is consistent with theoretical expectations
in most cases. However, Eq. 11 is probably not valid at low
stresses, so the present treatment is expected to break down at
some low stress value, apparently not yet achieved in static
fatigue experiments. The theory in its present form does not
demonstrate a fatigue limit at low stress; since soda-lime glass
samples aged in water become stronger, there must be a fatigue
limit at some low stress for this glass. However, previous
suggestions of fatigue limits in static fatigue or crack propa-
gation experiments disappear when the data are plotted according
to Eqs. 11 or 21.

Variations in t_n with sample history or between different
materials can only partly be explained by the present theory.

Previous theories also failed in this respect. Thus unknown factors change the sensitivity of samples to stress corrosion by water, even though the assumption that static fatigue results from stress-accelerated reaction of water with the material seems to be valid.

ACKNOWLEDGMENT

TABLE I

α/σ_t FOR DIFFERENT MATERIALS, CALCULATED FROM

STATIC FATIGUE MEASUREMENTS

Materials	Treatment	α/σ_t	Refs.
Soda-lime glass	Abraded	6.5	3, 10
(Kimble R-6)	Etched	11	5
Borosilicate Glass	Abraded	5.8	4
(G.E. FN,	Centerless		4
Corning 7050)	Ground	11.8	
Fused Silica	Centerless	} 7.4	4,9,10
(Amersil)	Ground, Pristine		
96% Alumina	As-received		
(Wesgo Al500)	Ground and Fired	} 21	4
	Fired only		

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TABLE II

LOG FAILURE TIME IN SECONDS AT $S/S_N = 0.5$ FOR VARIOUS
MATERIALS CENTERLESS GROUND OR ABRADED

Material	Treatment	Log t_n	Liquid Nitrogen Strength S_N MN/m²	(K psi)	Ref.
Alumina	Centerless Ground	4.8	520	(72)	4
Fused Silica	"	4.9	100	(15)	4
FN Borosilicate glass	"	1.5	100	(15)	4
Soda-lime Silicate glass	Various abrasions, aged in water	1.0 to -2.0	70 to 150	(10-22)	3,10

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TABLE III

RATES OF DISSOLUTION OF VARIOUS GLASSES AT 25 °C

Glass	Medium	Rate of Dissolution cm/sec.	Ref.
Silica	0.9% NaCl 0.1% NaHCO$_3$	$4(10)^{-13}$	24
	1M NaClO$_4$ in water	$3(10)^{-12}$	25
Lithium Silicate $\approx$25% Li$_2$O plus other oxides	water	10^{-13}	20
Soda-lime Silicate 15% Na$_2$O, 10% CaO	water	$2(10)^{-12}$ (extrapolated)	23

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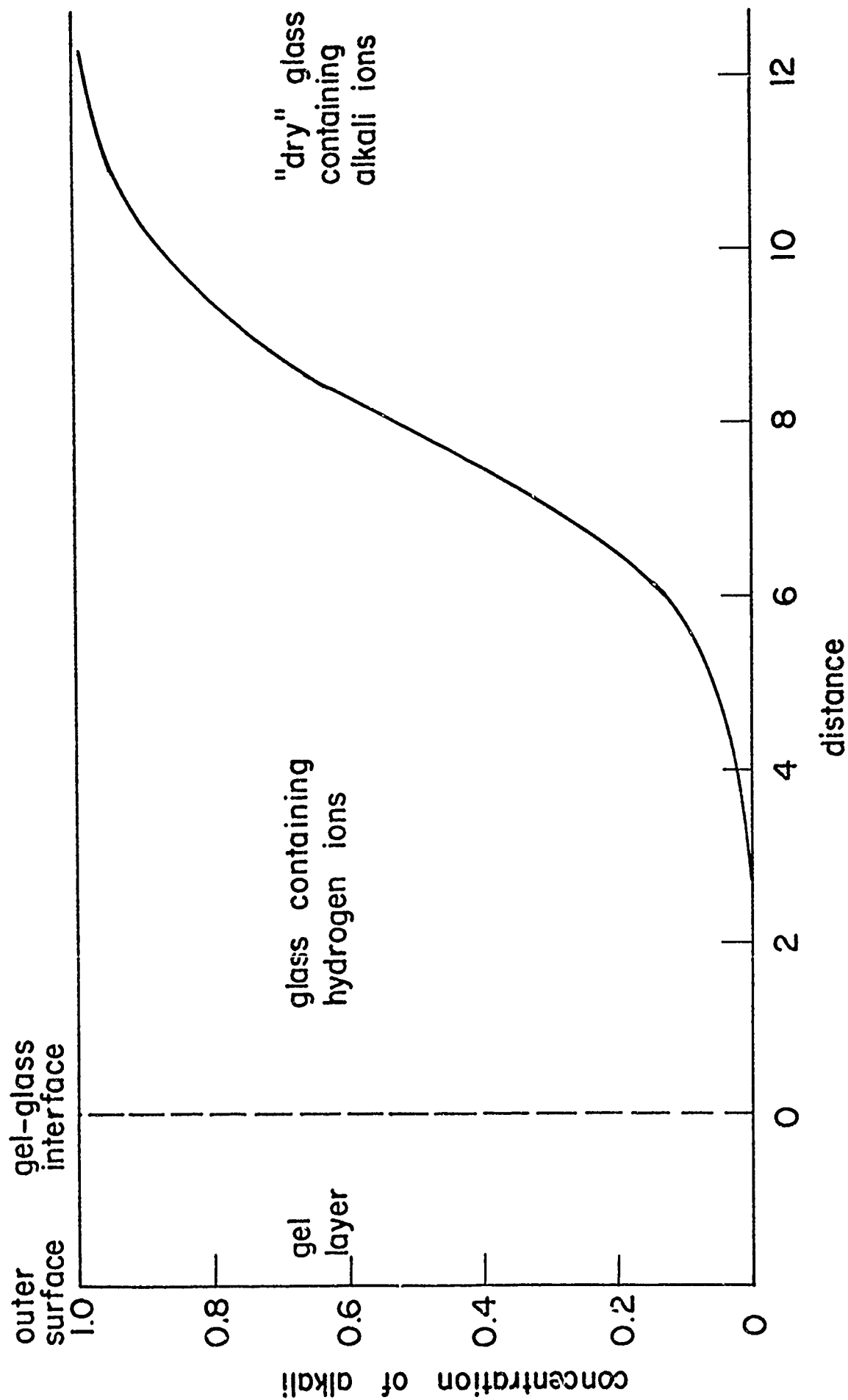
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Fig. 1   Schematic structure of the surface of an alkali silicate glass.

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CRACKS AND ENERGY - CRITERIA FOR BRITTLE FRACTURE

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INTRODUCTION

Brittle solids fail by propagation of flaws, usually in their surfaces. These flaws are thought of as thin, deep cracks penetrating from the surface into the solid. At the tip of such cracks any applied tensile stress becomes magnified, leading to propagation of the cracks at applied stresses S much lower than the ultimate or theoretical cohesive stress σ_t needed to break apart the solid.

Inglis[1] solved the elastic equations for an elliptical crack subjected to a tensile stress S perpendicular to the crack and found the stress σ at the crack surface to be:

$$\frac{\sigma}{S} = \frac{1 + 2c/a - (c+a)^2 \, x^2/a^4}{1 + (c^2-a^2) \, x^2/a^4} \qquad (1)$$

where c is the depth (semi-major axis) of the crack, a is the half-width (semi-minor axis), and X is the distance from the crack axis. At the crack tip X = 0, and:

$$\sigma_o = S(1 + 2c/a). \qquad (2)$$

If the crack is deep and thin c >> a, and:

$$\sigma_o \approx 2S \, c/a = 2S \, \sqrt{c/\rho} \qquad (3)$$

where $\rho = a^2/c$ is the radius of curvature at the crack tip. Even if the crack is not elliptical the tip stress is given by[1] $2S \sqrt{c/\rho}$. This relation shows that the stress at the tip of a deep, thin

crack is much greater than the applied tensile stress; this magnification explains the low fracture stresses of brittle solids compared to their theoretical cohesive strengths σ_t. The fracture stress S_f is

$$S_f = \sigma_t \sqrt{\rho} / 2\sqrt{c}. \tag{4}$$

. Griffith[2] calculated the strain energy $\mathcal{E}$ per unit length of an elliptical crack of depth c subjected to a tensile stress S and found that the crack lowered the energy of a stressed specimen by an amount, in plane stress:

$$\mathcal{E} = - \frac{\pi c^2 S^2}{Y} \tag{5}$$

where Y is Young's modulus for the material. Griffith assumed that the elastic energy released during crack propagation provides the additional surface energy of the growing crack, $4\gamma L$ per unit crack length, where γ is the surface energy, and derived the following equation (as modified by others) by equating the differentials of the two energies with respect to length:

$$S_f^2 = \frac{2Y\,\gamma}{\pi c} \tag{6}$$

where S_f is the applied tensile stress needed to propagate a crack or depth c.

A number of subsequent authors have used energy criteria to understand fracture and crack propagation. However, Eqs. 4 and 6 both profess to serve as criteria for fracture, and yet they are inconsistent. Various ways of reconciling these inconsistencies have been suggested[3,4].

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In this paper energies of crack propagation are considered in terms of the first and second laws of thermodynamics, and it is concluded that the Griffith criterion provides a necessary but not sufficient condition for crack propagation and failure, as suggested by Hillig[5]. An argument[3] to the contrary is considered, and surface energies of brittle solids, particularly oxides, are briefly discussed. Implications of the present view to experiments and theories on fracture are appraised.

FIRST LAW OF THERMODYNAMICS

The system under consideration is a block of material in a much larger solid subject to a uniform tensile stress S. One surface of the solid contains a thin crack of uniform dimensions along its length, which passes through the system or block. The crack extends much beyond the ends of the block, so there are no end effects. The outer dimensions of the block are assumed to remain constant with small changes in crack dimensions. The length of the crack from one face to the other is one length unit, so all energies are for unit crack length.

The first law of thermodynamics states that for a thermodynamic system there exists a state function E called internal energy such that

$$dE = dq - dw \tag{7}$$

where dq is the heat added to the system from the surroundings and dw is the work done on the surroundings by the system.

Temperature changes are usually negligible in elasticity

problems. As Timoshenko and Goodier point out[6], the difference

between the adiabatic and isothermal moduli of elasticity are small —

for iron the difference is 0.26%. Thus temperature changes in crack

propagation problems are often ignored, and only mechanical and

surface energies considered. I contend that temperature changes

during crack propagation cannot be neglected, and that they play an

important part in the energy balance of Eq. 7. There is no direct

experimental evidence to support or refute this contention. In an

attempt to measure the temperature change in glass near a propagating[7]

crack, a thermister placed a few tenths of a millimeter from the

crack path showed no change in temperature to within an accuracy of

a few tenths of a degree. However, temperature changes considerably

smaller than this would still play an important role in Eq. 7.

Two extreme possibilities are that crack propagation occurs

isothermally or adiabatically. If the process is to be isothermal,

heat must be added to or removed from the surroundings. Since the

crack propagates rapidly it seems more realistic to consider an

adiabatic process where no heat is exchanged with the surroundings

($dq = 0$) and the temperature of the material can change. In either

case if the system eventually reaches the same state the energy

change dE will be the same, since E is a state function.

Consider the changes in Eq. 7 as the depth c of the crack changes

adiabatically by dc. No external work is done on the system by the

surroundings, because the dimensions of the block remain constant

and there is no normal stress on the crack surface. Thus both dq and dw are zero, and all energy changes are changes in dE. The stored elastic energy $\mathcal{E}$ decreases by an amount:

$$d\mathcal{E} = -\frac{2\pi \, cS^2 \, dc}{Y} \qquad (8)$$

from Eq. 5. The surface increases by an amount 2dc per unit crack length, so the increase in surface energy is 4γ dc. The temperature of the material near the crack can increase or decrease; the amount of heat involved in this change is dQ, not to be confused with dq, the heat exchanged with the surroundings. Then F~ 7 becomes:

$$dQ - \frac{2\pi \, cS^2 dc}{Y} + 4\gamma \, dc = 0 \qquad (9)$$

Only if temperature changes are negligible (dQ = 0) can the Griffith equation, Eq. 6, be derived from Eq. 9. If the fracture stress is larger than predicted by Eq. 6, then $2\pi \, cS^2 \, dc/Y > 4\gamma$ dc, dQ is positive, and the temperature of the material near the crack increases. If $2\pi \, cS^2$ dc < 4γ dc, then the temperature decreases.

It is interesting to estimate the temperature change expected from a propagating crack. Consider a crack for which the Griffith fracture stress (Eq. 6) would be $70MN/m^2$ (10^4psi.). If the actual fracture stress is double this value, then about 20 joules of energy per cm^2 of crack surface formed are available for heating the sample. If the density is 2.5gms/cm^3 and the heat capacity 800 joules/gm$^{\circ}$C, a region half a millimeter thick at the crack surface will be heated about 0.1°C.

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The conclusion from this discussion is that a criterion for fracture can be derived from an energy balance alone only by assuming negligible temperature change, for which assumption there is no basis.

SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics can be stated for the present system as follows: For a single phase there exists a state function η called entropy such that

$$dE = - PdV + T\, d\eta + \gamma\, dA + d\mathcal{E} \tag{10}$$

when no mass is added to or subtracted from the system, and P is the pressure and V the volume of the system. A second part of the statement is that for any body consisting of one or more phases and isolated from the surroundings (E and V constant), the entropy of the body increases or remains constant according to whether the body is or is not in internal equilibrium:

$$d\eta \geq 0 \quad \text{(E and V constant)} \tag{11}$$

For the present system V is constant, so from Eq. 10:

$$T\, d\eta = dE - \gamma dA - d\mathcal{E} \tag{12}$$

Then from Eq. (9)

$$T\, d\eta = dQ \tag{13}$$

If the stress is lower than the fracture stress of Eq. 6, then the temperature of the material around the crack decreases and dQ is negative. However, this condition is contrary to Eq. 11. Thus crack propagation cannot occur for stresses below that predicted by

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Eq. 6, and this equation provides a necessary condition for crack propagation. This requirement based on the second law of thermodynamics was also recognized by Orowan[3].

It is interesting to inquire about what happens physically when the applied stress is high enough to cause propagation by Eq.4, but propagation cannot occur because S_f is lower than calculated from Eq. 6. The stress at the crack tip will be higher than the theoretical ultimate strength σ_t of the material; the material at the tip will fluctuate to a larger tip radius so that the tip stress is reduced below σ_t.

The minimum tip radius ρ_m for which fracture will occur can be found by equating Eqs. 4 and 6:

$$\rho_m = \frac{8Y\,\gamma}{\pi\sigma_t^2} \tag{14}$$

For fused silica, a representative brittle solid, Y is $7.2(10)^{10}$ N/m^2, and theoretical calculations give $\sigma_t = 1.8(10)^{10}$N/m^2 and $\gamma = 2.9$ J/m^2. Then from Eq. 14 ρ_m is about 16Å.

This discussion shows that any theory of fracture in which the tip radius of a crack is less than ρ_m cannot be correct. In particular some theories[8,9] have postulated a cusp-shaped tip, with an "infinite" radius of curvature. As soon as a tensile stress large enough to give a tip stress greater than σ_t is applied to such a crack, it fluctuates to a larger tip radius without propagating. Thus such a tip shape cannot be significant in crack propagation.

AN ARGUMENT TO THE CONTRARY

Orowan argued[3] that the Griffith criterion of Eq. 6 is both
necessary and sufficient, and tried to establish necessity from an
atomic model. The present arguments are entirely macroscopic, with
no recourse to an atomic model. Orowan assumed an intermolecular
stress-distance relation illustrated in Fig. 1. At low stress the
stress-displacement relation is linear (Hooke's law); as the
ultimate fracture stress is approached the stress for unit dis-
placement decreases. Orowan assumed that there is a region near
the crack tip where the stress is constant because of the failure
of Hooke's law at high stress. Neuber showed that if such a region
exists, the stress in it will be about the same as at the tip of a
crack of the same length and with a tip radius about the same as
the radius of the constant-stress region. If this radius is about
equal to the atomic spacing b, then from Eq. (4) the fracture
stress is

$$S_f = \sigma_t \sqrt{b}/2\sqrt{c} \tag{15}$$

Various equations for σ_t have been derived; Orowan used:

$$\sigma_t = \sqrt{2Y\gamma/b} \tag{16}$$

If this value is substituted into Eq. (15) the result is

$$S_f = \sqrt{Y\gamma/2c} \tag{17}$$

which is nearly the same as Eq. (6). Thus Orowan claimed that if
the applied stress is the value given by Eq. (6), the stress at the
tip of the crack will be σ_t, and failure will occur.

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Consider a crack of depth c with a tip radius $\rho \gg \rho_m$; in other words, a crack with a tip radius much greater than the value from Eq. 14 for the Griffith criterion to apply. Now increase the tensile stress S on this crack. When S reaches the value calculated from Eq. 6 the stress at the tip will still be much less than σ_t, so Hooke's law will hold around the crack tip. Only when the applied stress reaches a much higher value than calculated from Eq. 6 do deviations from Hooke's law appear. Thus the propagation stress for this crack is greater than predicted by Eq. 6, and Griffith's criterion fails. Orowan's argument applies only to cracks with tip radii <u>smaller</u> than ρ_m.

There is no experimental support for the stress-displacement curve shown in Fig. 1, although it is often used for theoretical calculations. Hillig[5] measured the stress-strain behavior of fused silica up to stresses close to the ultimate theoretical stress; the elastic modulus actually increased slightly at the highest stresses, and there was no indication of any decrease as predicted by the curve in Fig. 1. Thus there is no reason to expect a constant-stress region at the crack tip as postulated by Orowan.

SURFACE ENERGY

The surface energy γ used here may be considered to be one-half the energy needed to separate two atomic planes of unit area; it can be approximately calculated from th bond energy and atomic density of a solid. In this way γ values of 2.9 joules/m^2

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(2900 ergs/cm^2) for fused silica and 1.2 joules/m^2 for α-alumina

can be calculated.

In an actual fracture experiment surfaces formed may react

with ambient gases. Freshly fractured oxide surfaces are particu-

larly reactive; they form hydroxyl groups on their surfaces by

reaction with water, for example:

$$Si-O- + Si- + H_2O = 2SiOH \tag{18}$$
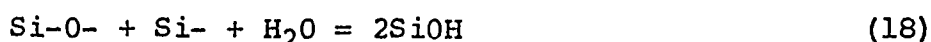
The surface energy of an oxide surface covered with hydroxyl groups

is much lower than calculated above. This is the reason that

measured values of surface energies of molten oxides are much

lower than the calculated values.

Nadeau[11] fractured glass cylinders at high stresses in

compression into fine fragments, and measured the heat given off

during fracture calorimetrically. The amount of heat given off was

not much less than the elastic energy stored in the glass just

before fracture. It seems likely that this heat results from the

exothermic reaction 18 occurring following fracture.

Surface energies have been calculated from fracture measure-

ments in several different ways[12-15]. In all of these methods the

Griffith relation (Eq. 6) is assumed valid. In one method the

stress needed to fracture a material with a crack of depth c is

measured, and the surface energy γ is calculated from Eq. 6:

$$\gamma = \frac{\pi S_f^2 c}{2Y} \tag{19}$$

In the present view the stress needed to propagate a crack of length c will be greater than or equal to the value calculated from Eq. 6. Thus one might expect values of γ calculated by these methods to be larger than the theoretical values and scattered. These are the results found experimentally. γ values for sapphire[16] range from 6.0 to 32 j/m^2; for polycrystalline alumina[14,16], from 18 to 54 j/m^2; for soda-lime glass[15,17], from 3.4 to 11 j/m^2; for magnesia[13] from 1.1 to 3.0 j/m^2. It seems reasonable to conclude that the lowest value for each material gives only an upper bound to the "true" surface energy.

DISCUSSION

Brittle solids fail because of the magnification of stress at the tips of thin, deep cracks (Eq. 3). Thus it is not surprising that Eq. 6, in which this magnification plays no role, cannot provide a criterion for fracture. In the integration to calculate the change in elastic energy caused by the presence of the crack (Eq. 5) the terms involving the high stress at the crack tips are negligible, because the volume over which this high tip stress occurs is very small, and becomes smaller as the tip stress increases

In a brittle material some surface cracks can have the minimum radius ρ_m given by Eq. 14, because cracks starting with smaller radii will fluctuate to this value as soon as the required stress is applied. Thus in many instances brittle materials with cracks of depth c will fracture at the minimum stress as calculated from Eq.6.

In some experiments on fracture of soda-lime glass [18] the crack depth

was measured from etching experiments and the tip radius calculated

to be about 20Å. This is close to the radius calculated from Eq.

14, so the Griffith equation (Eq. 6) should apply in this case.

However, when this glass was treated in water its strength increased,

yet the crack length remained the same[19]. In this case the Griffith

equation was not obeyed, and the tip radius was calculated to be

33Å, or considerably greater than the value from Eq. 14. These

results emph size that in fracture experiments the tip radius of

the crack is a parameter that cannot be ignored, as is done in an

energy approach; Eq. 3 provides the correct criterion for crack

propagation and failure, not Eq. 6.

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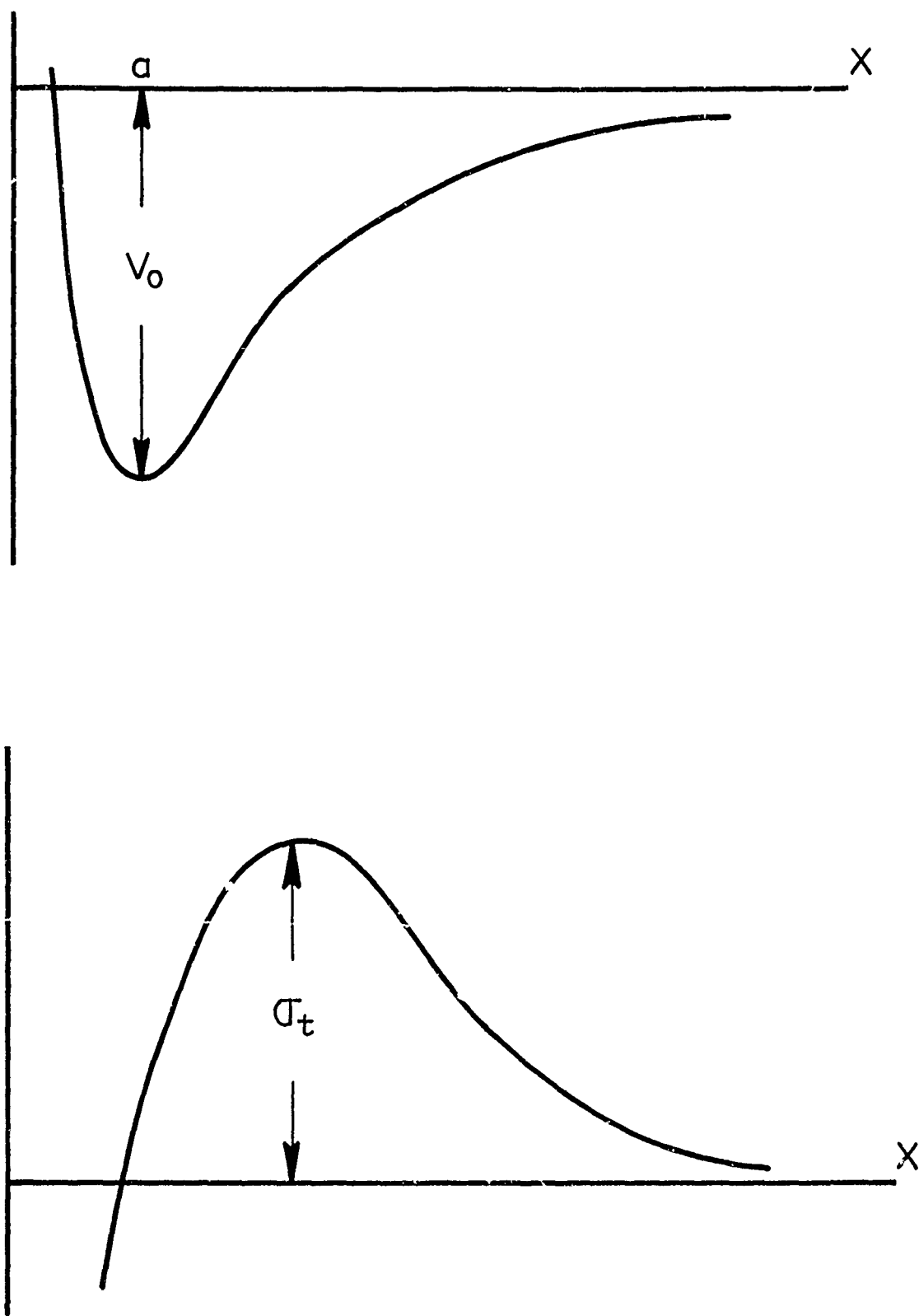19. R. H. Doremus and E. K. Pavelchek, to be published in J. Appl. Phys.

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Fig. 1 Theoretical stress-displacement curve for atomic bonds.

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